# Vibrational Spectra of 2.6-Iutidine in Liquid Phase and Orientationally - Arranged Wall - Adjacent Layers<sup>1</sup>

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**ABSTRACT** 

Dispersed phase as a state of the heavy particles surface determines to a

great extent the physical properties of the boundary liquid layers that are of

great importance for the kinetics of such processes as coagulation, wetting, the

processes of aerosol particles trapping, etc.

The electronic vibrational spectra of 2.6 - Lutidine in the frequency region

v = 30000 - 47000 cm<sup>-1</sup> - were investigated. The form and main parameters of five

symmetrical bands were determined.

Absorption spectrum of ultrathin wall - adjacent orientationally-ordered

layers (with thickness d ≤ 300 nm formed near lyophilic quartz surface (so called

epitropic liquid crystals - ELC) essentially differs from the bulk one and alters with

the thickness decreasing. In particular the halfwidth of intermolecular charge

transition band decreased and the bathochromic shift was observed.

Given is a critical analysis of the existing colloidochemical theories of the

orientation of epitropic liquid crystals on solid surfaces.

KEY WORDS: epitropic liquid crystals, orientation, vibrational spectra.

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### 1. INTRODUCTION

The boundary phases investigated nonmesogenic of organic liquids in view of existence in them distant orientation of the order naturally should be related to a liquid crystal condition, and as symmetry to nematic liquid crystals. However, as against usual thermotropic liquid crystals, orientation homogeneity of boundary phases can arise only in a field of superficial forces liophilic of a firm substrate. Therefore, by analogy to the established terminology, such special boundary phases of organic liquids with induced by superficial forces orientational arrangement of molecules in them were named in [1] epitropic liquid crystals (ELC). Distinctive feature epitropic of liquid crystals is their spatial limitation and opportunity of equilibrium existence ELC of a phase with a volumetric liquid in a significant interval of temperatures. The decrease of equilibrium thickness ELC of a phase with growth of temperature with simultaneous reduction of a degree ordering in it testifies about gradual orientation melting ELC of phase.

Earlier [2-4] we investigated the characteristics orientational of ordering in boundary ELC-layers lutidine and the character of their change with growth of temperature is determined. Was established, that on a surface of quartz lutidine, as well as other organic liquids, will form orientationally ordered structures boundary ELC-layers.

It has become obvious, that the field of superficial forces, alongside with other factors responsible for organization ELC, by virtue of the heterogeneity reduction of potential with distance from a substrate - should result and in the certain heterogeneity of physical properties within the limits of each of phases. Therefore it is necessary to expect and monotonous change some structural - sensitive of properties such wall adjacent layers in process of increase of distance up to substrate.

For an establishment of heterogeneity structure within the limits of ELClayer and its interrelation with potential of a field of superficial forces, we have carried out researches of changes in vibrational spectra of ELC-phase 2.6lutidine formed on a surface of quartz, in process of increase of thickness of a liquid layer.

## 2. EXPERIMENT

We investigated more thin wall adjacent area of liquid layers 2.6 lutidine. The structure with a higher degree orientational ordering in a ELC-layer was established. Similar quasismectic structural ordering see and our colleagues with research of boundary layers nitrobenzene of variable thickness 5-20 nm [5].

For research of spectra absorption in the field of wave numbers  $v = (30 \div 47) \cdot 10^3$  cm<sup>-1</sup> was used "Specord-M40", allowing to carry out analog and numerical records of spectra with their subsequent machine processing. The accuracy of reproduction of wave number in the specified range is not worse  $\Delta v \approx 5$  cm<sup>-1</sup>, the resolution makes ~ 10 cm<sup>-1</sup>, and accuracy of measurement of intensity -  $\Delta I/I \approx (0.005 \div 0.001)$ .

Notwithstanding what earlier [5] was already studied more long -  $\nu$  =  $(25 \div 40) \cdot 10^3$  cm<sup>-1</sup> a range of an electronic spectrum of absorption for nitrobenzene, by us the spectral measurements of solutions 2.6-lutidine in a polar solvent - water were carried out. The set quartz two substrates with backlashes 5-40 microns was applied to these measurements.

#### 3. MEASUREMENTS OF THE VIBRATIONAL SPECTRA

For research of a spectrum of a ELC-phase in process of change thickness a liquid layer the technique [1] scanning in thickness of a layer the liquid formed between optical by polished quartz substrates was used. The topography of a backlash was defined previously (before filling by its preparation) interferometry in taking place light on several lengths of waves near atmospheric ultraviolet of a range. The rules extremums interferensial bands of a picture have allowed enough above to restore a structure of a backlash down to thickness of a layer

25 nm. After filling cuvette the liquid carried out research of absorption on frequency of a maximum of the band, brightly expressed in a spectrum, - intermolecular carrying of charge (ICC -  $v_0 \approx 38000$  cm<sup>-1</sup>). The intensity of taking place light as function of thickness of a layer d was measured and the dependence InI = f (d) was under construction which looked like convex broken (see fig. 1). The analysis allowed last (on inclinations of its pieces) to establish meanings of linear factors of absorption ELC ( $\mu_s$ ) and bulk ( $\mu_{iso}$ ) of a phase, phase uniformity (on a degree of affinity of sites of the diagram to linear) to calculate scalar parameter of the order S and to determine thickness of a phase (on coordinates of a point of a break).

Further for this of layer liquid the measurements of spectra - dependencies of optical density D = In  $(I/I_0)$ , where I and  $I_0$  - intensity of light, past accordingly through a layer researched lutidine and through a layer of a not absorbing liquid filling a backlash between the same substrates from frequency of falling light (were carried out). Each of measurements corresponded to various thickness of a liquid film in a range 25-300 nm. In a case two-phase of a layer (d = 100 nm) spectra of absorption isotropic of a volumetric phase in addition were determined difference spectra, and then the basic series of spectral measurements was carried out within the limits of thickness of a ELC-phase of a fig. 1.. For the further analysis the decomposition of an experimental spectrum on elementary bands by analogy to the described circuit [5] for nitrobenzene was carried out. An opportunity of approximation of the form of spectral bands Lorentz or Gaussian by functions with the help them linearization and check on linear previously was checked. As was established, the form long-range band of a slope band ICC is determined Gaussian. Further, for a finding of parameters of a band - factor of absorption (m<sub>0</sub>) appropriate to frequency of a maximum of a band of the absorption n₀ and half-width of the band (s), the parameters of linear dependence paid off

$$\left(\ln\frac{\mu_0}{\mu}\right)^{\frac{1}{2}} = f(\nu) \tag{1}$$

Further, the reproduced band was subtracted from an experimental spectrum, and the similar method determined the form and parameters of the subsequent spectral bands. The described method allowed to carry out decomposition with the incomplete information on a spectrum and to allocate a line weak, disguised bands.

However given approach has line of restrictions connected that on a site linear one band should dominate only (i.e. the contribution of the next bands should be negligible), that not always it is possible. Besides because of narrowness the area of a linear spectral interval (1) criteria determining it of border, insufficiently statistically are reasonable. Therefore specification of the form and parameters with the help of a stricter method described in [5] further was carried out.

Let spectrum f (v) consists from n of symmetric bands  $\phi$  (v):

$$f(\nu) = \sum_{i=1}^{n} \phi_i(\nu) \tag{2}$$

Using a condition of symmetry

$$\phi_{i}(\mathbf{n}) = \phi_{i}(2\mathbf{v}_{0i} - \mathbf{v}), \tag{3}$$

Where  $\nu_{\text{oi}}$  - rule of a maximum i- of a band, the following iterative process on a finding of the form of elementary bands was under construction:

$$\phi_{k}^{(j)} = \frac{1}{2} \left[ f(2\nu_{oi} - \nu) + f(\nu) \right] - \frac{1}{2} \sum_{k=1}^{n} \left[ \phi_{k}^{(j)} (2\nu_{oi} - \nu) + \phi_{k}^{(j)} (\nu) \right] - \frac{1}{2} \sum_{k=i+1}^{n} \left[ \phi_{k}^{(j-1)} (2\nu_{oi} - \nu) + \phi_{k}^{(j-1)} (\nu) \right]$$
(4)

The iterative procedure (4) is similar to a method Zeidelia, frequently used for the decision of system of the linear equations. The numerical experiments which have been carried out on model systems, show, that the process converges irrespective of a choice of initial approximation. However it is not enough

of one level of symmetry for reception of unequivocal decomposition - the additional information on the form of bands is necessary. If the specific form of elementary bands (for example, close to gauss) is known, the unequivocal decomposition can be received according to the following algorithm: 15-20 iterations will be carried out, then approximation the form of elementary bands Gauss by curves and again will be carried out specification of their form under the circuit (4). The process proceeds so long as with the given accuracy the parameters of bands (width and intensity) will not cease to vary.

#### 4. RESULTS

General view of a spectrum and the results of its decomposition on elementary bands are given on fig.2. In an experimental spectrum the bands ICC (2) and second primary (b-band lutidine ,  $v_0 \sim 38000~\text{cm}^{-1}$ ) are precisely allocated, and also is visible band with  $v \sim 47000~\text{cm}^{-1}$  (4), almost completely disguised by a stronger b-band (5). The bends with maxima  $v_0 \sim 33000~\text{cm}^{-1}$  (1),  $v_0 \sim 42500~\text{cm}^{-1}$  (3) are completely disguised and can be found only during decomposition of an experimental spectrum. According to the literary data the band with  $v_0 \sim 33000~\text{cm}^{-1}$  (1) corresponds to intermolecular carry of a charge and consequently low-intensity even in the concentrated solution.

In a fig. 1. the dependence LnI = f (d) is shown, which analysis has allowed to determine thickness orientationally of the ordered boundary ELC-layer (d<sub>s</sub> ~ 35 nm), factors of absorption in a volumetric phase and wall adjacent liquid layer ( $\mu_{iso} \cong 6.5\mu$ –1 and  $\mu_s \cong 5.3\mu$ –1) to calculate parameter orientationally ordered S (S  $\leq$ 0.2).

The orientation of molecules of a liquid (is exacted dipole of the moment of electronic transition in molecules appropriate to a maximum of a main band of absorption  $v_0 \sim 38000$  cm<sup>-1</sup> is homeotropic. Dependence represented in a fig. 1., has the same kind as well as for other liquids monoreplaced benzene (for ex-

ample, nitrobenzene), but the parameters ds and S for nitrobenzene are little bit higher: ~ 60 nm and 0.3, accordingly. A spectrum of absorption lutidine in ultraviolet of area of a spectrum of a fig. 3. Has the isolated band about (38000 cm<sup>-1</sup> ). The short-wave part of a band is non-uniform widening, that testifies to presence additional, disguised bands. Long-wave the slope of a band was normalized and was compared with Gaussian by a curve. The faster decrease of experimental dependence compared with model Gaussian serves the additional proof of complex structure of a band intermolecular of carry of a charge about  $v_0$ ~38000 cm<sup>-1</sup>. In long-wave part of a spectrum there is low-intensive a band about (v<sub>0</sub>~33000 cm<sup>-1</sup>) with the advanced oscillatory structure and in short-wave - intensive benzene about  $v_0$ ~49000 cm<sup>-1</sup>. The spectra were decomposed on symmetric gauss of a band, the number and which probable rule was determined from the analysis of derivative spectra. The parameters of elementary bands half-width  $\delta$ , intensity were determined, frequency  $v_0$ , changes of parameters with thickness and temperature further were analyzed. Registration of vibrational spectra of own absorption (in a range of frequencies  $v_0 \sim 30000$  cm<sup>-1</sup> -4700cm<sup>-1</sup>) and subsequent their analysis were carried out for layers of a liquid by thickness 1 - 80 nm, i.e. in the field of thickness of a wedge appropriate to a single-phase condition lutidine, with which orientational - ordering wall-adjacent layers are not divided by a layer isotropic of a volumetric liquid phase. Spectral of change with thickness of a film I brightly were displayed in change of halfwidth  $\delta$  (band with a maximum  $v_0 \sim 43000$  cm<sup>-1</sup> a fig. 3. The parameters of the next bands changed within the limits of a mistake. With growth of temperature was observed bathochromic shift of a maximum of a band  $v_0$ ~38000 cm<sup>-1</sup>. The effect of heating is equivalent to a thickening of a film, i.e. downturn of a degree ordering. With increase of temperature dispersion of elementary bands change poorly, the frequencies - are displaced: for elementary bands with a maximum  $v_0 \sim 37000$  cm<sup>-1</sup> and 40000 cm<sup>-1</sup> - shift batochromic, and for bands with

a maximum  $v_0$ ~43000cm<sup>-1</sup> and  $v_0$  ~ 41000 cm<sup>-1</sup>. shift in other party. And for bands " of a doublet  $v_0$ ~37000cm<sup>-1</sup> and  $v_0$ ~40000cm<sup>-1</sup> with change of temperature relative intensity the component and shift them on frequency rather each other practically does not change. The parameters of a band with a maximum  $v_0$ ~33000cm<sup>-1</sup> were not analyzed, as small their intensity determined large size of an error.

Is established, that with transition from pair to a solution 2.6-lutidine and, accordingly, to increase of intermolecular interaction the band ICC tests bato-chromic shift, and for other bands the displacement insignificantly and lays within the limits of mistakes of experience.

Is shown, that for anisometric of molecules lutidine, having significant dipole by the moment ( $P_e(D) = 2,20$ ), the contribution orientational of interaction in size of shift of frequency is comparable with the total contribution of all other interactions.

In a fig. 5 a series spectra of absorption symmetric layers 2.6-lutidine is submitted appropriate to various thickness of a ELC-phase. As it is visible from a figure, in process of reduction of thickness of a layer the band  $v_0$ ~47000cm<sup>-1</sup> becomes more and more detached at the expense of change parameters the next bands, and also the rule of a maximum of half-width of the most intensive of them - band ICC changes. Parameters of separate spectral bands for several thickness of a layer appropriate to a condition (d < 100 nm). For other bands the observable changes have that a direction, however are expressed less distinctly in connection with smaller intensity and decrease of reliability of received results on the top border of a researched spectral range.

Graphically results of change of parameters of a band ICC -  $\Delta v$  (shift of frequency a maximum) and its half-width - as functions of thickness d of a layer ELC are submitted in a fig. 6 a, b.

The observable spectral changes are caused by change of structural parameters of a ELC-phase with distance from a substrate, that is at the end determined by change of size of potential of superficial forces. The reduction of half-width of a line, apparently, testifies to increase of a degree ordering of system and can be connected to increase of parameter of the order answering for dispersion of ordering molecular axes. The observable frequency displacement is caused by influence of superficial forces of a substrate on structure of a ELC-phase.

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#### FIGURE CAPTIONS

- Fig. 1. Experimental dependence of absorption of light 2.6-lutidine in cuvette a maximum of a band intermolecular of carry of a charge.
- Fig. 2. A spectrum of absorption lutidine in ultraviolet of area a spectrum
- Fig.3. Change dispersion of a band 43000 cm<sup>-1</sup> depending on thickness of a layer 2.6-lutidine
- Fig.4. An experimental spectrum of absorption 2.6-lutidine and its decomposition on elementary bands 1-5.
- Fig.5. Experimental spectra of absorption wall-adjacent layers 2.6.-lutidine for various thickness d (nm) of layers of a liquid, d: 300 (1), 183 (2), 100 (3), 85 (4), 60 (5).
- Fig. 6. Dependencies of shift of a maximum  $\Delta v$  ICC of a band of absorption a ELC-phase 2.6-lutidine (concerning a rule of a maximum  $v_0$  about by of a bulk liquid) (a) and of half-width  $\sigma$  (b) from thickness of a layer of a preparation (d).













